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FR-A- 2 334 699	GB-A- 2 104 085
US-A- 3 925 582	US-A- 4 719 132

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Description**BACKGROUND OF THE INVENTION**

Multi-layer systems have been utilized to coat automobiles for a number of years, but the early development of these systems necessarily employed organic solvents. As environmental regulations became more stringent, and the cost of organic solvents rose, organic-borne systems became less desirable. The recent research emphasis in the area of multilayer systems, especially basecoat systems has focused on the development of water-borne systems for multi-layer coatings.

The shift from organic solvents to water for dispersing and applying resins in multi-layer systems solved many of the environmental and cost problems associated with the use of organic solvents. Water-borne systems, however, have resulted in other problems.

One solution to these problems has been the development of anionic polyurethane resins as described, for example, in US-A-4,791,168. These resins exhibit superior coating characteristics in many basecoat/clearcoat multi-layer systems. However, in certain instances these resins may not be compatible with strong acid catalyzed high-solids melamine-containing clearcoats, because of the tendency to exhibit wrinkling, and loss of DOI (Distinctness of Image); especially when light colored pigments (white, light blue, yellow) are used.

The polyurethane resins of the present invention, however, may be used in the above-described melamine-containing systems without the negative characteristics exhibited by anionic resins. Thus, the combination of non-ionic polyurethane basecoats with strong acid catalysed clearcoats allows for a lower composite Volatile Organic Content (VOC) than with anionic polyurethane basecoats.

In a further aspect of the present invention nonionic polyurethane resins are formulated into grind resins for use in basecoats. Yet, aqueous dispersions of nonionic polyurethanes are known in the literature and have been used to prepare films and coatings. Generally, polymer dispersions are unsuitable for use in milling pigments. It is quite surprising that the aqueous dispersions of the nonionic polyurethanes of the present invention are effective grind resins for a wide variety of pigments.

FR-A-2 222 404 discloses dispersions of non-ionic polyurethanes prepared without the use of emulsifying agents. GB-A-2 104 085 discloses aqueous dispersions of crosslinked urea urethane polymers and their method of production. FR-A-2 235 668 describes a process for the preparation of polyurethanes by the production of aqueous dispersions of polyurethane prepolymers. US-A-3 925 582 discloses the production of terminally stabilised polyurethane resins. FR-A-2 334 699, EP-A-269 972 and EP-A-0 242 731 describe the preparation of water dispersible polyurethanes. US-A-4 719 132 is related to a process for producing multi-layered coated articles. The process comprises applying a pigment containing aqueous polyurethane film-forming composition to a substrate to form a basecoat followed by the application of a transparent topcoat to the basecoat.

The present invention is directed to a method of coating a substrate with a multi-layer coating comprising

(A) applying onto the substrate a first layer of waterborne basecoat composition comprising

a) a water-dispersible polyurethane resin wherein said polyurethane resin has an hydroxyl value of at least 5 and comprises the isocyanate group-free reaction product of

I) a polyurethane resin having at least some free isocyanate groups that is the reaction product of

1) at least one polyester polyol, and optionally at least one diol and/or triol having hydroxy values of 200 or above

2) at least one nonionic stabilizer that is a monofunctional polyether or is the reaction product of i) a polyether half-capped diisocyanate intermediate formed by the reaction of a monofunctional polyether with a diisocyanate, and

ii) a compound having at least one active amine hydrogen reactive with isocyanate groups and at least two active hydroxyl groups reactive with isocyanate groups, and

3) an excess of at least one polyisocyanate, and

II) at least one diol, triol or aminoalcohol capping agent to cap said free isocyanate groups, and

b) an aminoplast resin or a polyisocyanate crosslinking agent, and

(B) flash drying said first layer within a temperature range of room temperature to 63 °C,

(C) applying at least one layer of a clear top coat onto said basecoat, and

(D) baking said multi-layer coating to crosslink the coating to a hard durable film.

Coatings prepared by the method according to the present invention exhibit superior coating characteristics, for example, good metallic effects such as very favorable arrangement, fixation, and flip effect of the metallic pigments in the paint film. When non-metallic pigments are used, the coatings prepared by the

method according to the present invention exhibit a high level of decorative effect.

SUMMARY OF THE INVENTION

Two types of polyether-containing polyurethane resins are used according to the present invention. We have termed these two types of resins laterally stabilized and terminally stabilized.

Specifically, this invention relates to the use of a laterally stabilized polyurethane coating composition in a method of coating a substrate with a multi-layer coating. This laterally stabilized polyurethane is comprised of:

1. at least one organic compound having at least two reactive hydrogen atoms;
2. a nonionic stabilizer prepared by the reaction of:
 - i) a monofunctional polyether with a first polyisocyanate-containing compound to produce a partially capped isocyanate intermediate; and
 - ii) a compound having at least one active amine hydrogen and at least two active hydroxyl groups; and
3. at least one second polyisocyanate-containing compound.

The organic compound preferably comprises a polyester polyol, a low molecular weight diol/triol or mixtures, thereof. A capping agent is employed to cap any remaining free isocyanate moieties.

In addition, this invention also relates to the use of a terminally stabilized polyurethane coating composition in a method of coating a substrate with a multi-layer coating. This terminally stabilized polyurethane is comprised of:

- 1) at least one organic compound having at least two reactive hydrogen atoms;
- 2) a monofunctional polyether; and
- 3) a polyisocyanate.

The organic compound of the terminally stabilized polyurethane preferably comprises a polyester polyol, a low molecular weight diol and/or triol, or mixtures thereof. Optionally, a separate trifunctional hydroxyl-containing monomer is employed for use in the polyurethane resins of the present invention. A capping agent is employed to cap any remaining free isocyanate moieties.

In the laterally stabilized polyurethane resins, the incorporation of the polyether groups functions to chain extend the polyurethane resin. In contrast, the incorporation of the polyether groups in the terminally stabilized polyurethane resin functions to terminate the resin. The two types of polyurethane resins described above can be formulated as a water-dispersed basecoat composition which contains in addition to either of the above-described resins a grind resin, a cross-linking agent, thixotropic or rheology control agents, thickeners, pigments, aluminum and/or mica particles, basifying agents, water, fillers, surfactants, stabilizers, plasticizers, wetting agents, dispersing agents, adhesion promoters, defoamers, catalysts, and additional polymers.

In preferred embodiments of basecoat compositions used according to the present invention, the terminally stabilized polyurethane resin is utilized as the principle resin and the laterally or terminally stabilized polyurethane resins is utilized as the grind resin.

After formulation, the basecoat composition can be sprayed or deposited onto an automobile body, preferably, in one or two coats. Generally, two even coats of basecoat are applied with a several minute flash between coats. After deposition of the basecoat, before application of a high solids content clear coat, it is generally preferred to flash about 90% of the water from the basecoat for optimum appearance and to eliminate water boil of the clearcoat.

In both the linear and branched chain polyurethane resin, a polyester polyol resin is a major component.

The polyester polyol resins described hereinabove are themselves useful on virtually any elastomeric substrate, but they are particularly useful when formulated into polyurethane coatings and used in basecoat formulations for deposition onto metal or plastic substrates, especially automobile bodies.

The polyester component may be any type, i.e., branched or unbranched, and is formed from the reaction of at least one dicarboxylic acid component and at least one alcohol component wherein the alcohol has at least two hydroxyl moieties.

Virtually any carboxylic acid-containing compound having two or more carboxylic acid moieties or equivalents that are useful in synthesizing polyester compounds are useful in the present invention.

The carboxylic acid component may, of course, be comprised of short-chain dicarboxylic acid compounds, long chain dicarboxylic acid compounds, or mixtures thereof. By short chain dicarboxylic acids we mean compounds having at least two carboxylic acid moieties and fewer than 18 carbon atoms in the chain. These dicarboxylic acids may be alkyl, alkylene, aralkyl, aralkylene, and arylene. In the polyester

resins of the present invention the carboxylic acid containing compound may be polyfunctional with 2 or more carboxy groups. A preferred carboxylic-containing compound for use in branched polyester resins is trimellitic anhydride. Short-chain alkyl or aryl dicarboxylic acid compounds for example azelaic acid, adipic acid, or an equivalent aliphatic or aromatic acid are preferred. A preferred aromatic dicarboxylic acid is isophthalic acid.

The carboxylic acid component may also be comprised of a long-chain dicarboxylic acid component. This long-chain dicarboxylic acid containing compound may be an alkyl, alkylene, aralkyl or aralkylene compound, but it must be stressed that virtually any long-chain dicarboxylic acid containing compound may be used. An especially preferred long-chain carboxylic acid-containing compound is C36 dicarboxylic acid known as dimer acid. A discussion of dimer acid can be found in US-A-4,791,168. As in the case of the short-chain dicarboxylic acid-containing compounds, linear dicarboxylic acid-containing compounds may be preferably used in linear polyurethane resins, and linear or branched dicarboxylic acid-containing compounds may be preferably used in branched chain polyurethane resins.

In addition to the carboxylic acid containing compound, the polyester resin is also comprised of one or more low molecular weight diols or triols. We have termed any compound having more than one alcohol group a polyol. Polyols may be diols (di-alcohol containing), triols (tri-alcohol containing) or higher alcohol-functional compounds in the case of the branched-chain polyurethanes, the amount and type of triol-containing compounds may be varied to increase the branching effect. A preferred trialcohol-containing compound for use in the branched chain polyesters is trimethylol propane.

The polyester resin or mixture of polyester resins utilized to synthesize the polyurethane resins preferably are hydroxyl terminated. This is effected by synthesizing the polyester using an excess of a diol or triol-containing compound. The relative weights of the carboxylic acid component and alcohol-containing compound depend upon the desired chain length of the polyester compound employed. The result of this synthesis is a polyester having two or more free hydroxyl groups (polyesterdiol or polyol).

The composition of the carboxylic acid component and polyol component employed to synthesize the preferred polyester resins is such as to provide an excess of the polyol over and above the total number of equivalents of acid present in the mixture. In other words, the reactants should be selected, and the stoichiometric proportions of the respective acid and polyol components should be adjusted to give hydroxyterminated, polyester molecules each theoretically having a hydroxyl functionality of 2 or more.

Monocarboxylic acids and monoalcohols may also be used in the polyester synthesis, but these are generally utilized for the purpose of chain terminating a polyester resin. As a general rule, where used, the monocarboxylic acids and/or monoalcohols comprise a very small percentage by weight of the final polyester resin.

As a general rule the polyester diol component comprises between about 20% and 80% by weight of the final polyurethane resin. Preferably the polyester diol comprises between about 50 and 70% by weight of the polyurethane resin and most preferably the polyester diol comprises between about 55 and 65% by weight.

While it is recognized that almost any size chain length of polyester polyol can be utilized, it is preferable to use a polyester diol within the molecular weight range of between 500 and 5000. It is preferable that the molecular weight range of the polyester diol component be between 1,000 and 3,500.

In addition to the polyester diol, the polyurethane resins of the present invention are also comprised of additional organic compounds having at least two reactive hydrogen atoms. This component is preferably a low molecular weight diol or triol compound but may contain alcohol groups, thiols and/or amines or mixtures of these functionalities. The same alcohol-containing compounds utilized to synthesize the polyester-containing compound may be utilized as a separate component here. Thus, any di or tri-alcohol containing compound may be used, for example neopentyl glycol and 1,6 hexanediol. High molecular weight diols and triols are not preferred, however, where the hydrophobicity of their molecular chains impacts on the water-dispersibility of the final polyurethane resins. The purpose of this alcohol containing component is to provide chain extension and/or branching through the isocyanate containing compounds. Thus, depending upon the desired amount of chain extension and/or branching desired in the final polyurethane resin, varying weight percentages and types of diols and/or triols may be utilized. Where linear polyurethane resins are desired the ratio of diol-containing compounds to triol-containing compounds may be higher than when branched chain polyurethane compounds are desired.

The amount of low molecular weight diol and/or triols utilized in the polyurethane resins of the present invention may vary between 0 and 20 percent by weight of the polyurethane resin. Preferably this low molecular weight alcohol component comprises between 0 and 10 percent of the polyurethane resin and most preferably comprises between 1 and 6% by weight of the polyurethane resin.

The polyurethane resins of the present invention further comprise a polyisocyanate, preferably a diisocyanate. Generally, the diisocyanate comprises between 5 and 40% by weight of the final polyurethane resin. Preferably, the diisocyanate comprises between 10 and 30 percent by weight of the final resin and most preferably comprises between 10 and 20 percent by weight of the polyurethane resin.

5 A polyether-containing compound provides the polyurethane resin with the preferred water dispersibility characteristics. These water-dispersibility characteristics are inured to the polyurethane resins of the present invention without the need to incorporate salt-forming groups within the resin. The absence of salt-forming groups enables the polyurethane resins to be incorporated into basecoat compositions which may be utilized in combination with strong acid catalysed high solids melamine-containing clearcoats. This results in
10 a lower composite VOC coating which does not exhibit the same wrinkling, loss of DOI (Distinctness of Image) and "browning" effects shown by the cation-containing polyurethane resins.

Two different approaches for incorporating polyether segments into the polyurethane resins are available depending upon the type of polyurethane resin desired. The approach to synthesizing a laterally stabilized polyurethane utilizes a polyether diol prepared from the reaction of a monofunctional polyether
15 with a diisocyanate to form a polyether half-capped diisocyanate. This half-capped diisocyanate is then reacted with a compound having one active amine hydrogen and at least two active hydroxyl groups to form a non-ionic stabilizer (polyether diol) having a polyether chain, a urea moiety, a urethane moiety, and two free hydroxyl groups.

Once synthesized, the non-ionic stabilizer is then added to a reaction mixture comprised of at least one
20 organic compound having two or more reactive hydrogen functionalities, and an excess of a polyisocyanate-containing compound (in addition to that which is incorporated into the nonionic stabilizer). Preferably a polyester polyol is also added to form the polyurethane. A capping agent, for example, trimethylol propane or diethanolamine is used to cap any remaining free isocyanate groups. The resulting laterally stabilized polyurethane resin may be formulated in a basecoat composition and is preferably utilized as a grind resin.
25 The laterally stabilized polyurethane resin may also be formulated as a principal resin, but for purposes of the present invention, the terminally stabilized polyurethane resin is preferably utilized as the principal resin, and can also be used as a grind resin.

The polyether component which instills water-dispersible characteristics to the laterally stabilized and the terminally stabilized branched-chain polyurethane resin is a polyether having one functional group, for
30 example methoxypolyethylene glycol. The polyether component is generally produced by utilizing a monoalcohol initiated polymerization of ethylene oxide, propylene oxide or mixtures thereof. The functional group on the polyether compound may be any group reactive with isocyanates to form a stable product. Thus, the polyether compound may contain a free hydroxyl, thiol, or amine, but hydroxyl functionalities are preferred to minimize the possibility of salt formation.

In the laterally stabilized polyurethane resin, the monofunctional polyether compound is, as previously described, reacted with a polyisocyanate-containing compound to form a half-capped isocyanate. This half-capped isocyanate is then reacted with a compound having an amino active hydrogen and at least two free hydroxyl groups (or equivalent functionalities). This resulting product, termed the nonionic stabilizer, is then incorporated into the polyurethane resin by reaction with the other components. In contrast, in the terminally
40 stabilized polyurethane resin, the polyether functionality is incorporated into the resin as the monofunctional polyether.

The monofunctional polyether compound is reacted with a mixture comprised of at least one polyester polyol, a polyisocyanate, and in addition, optionally a short chain low molecular weight diol or higher functional polyol, or mixtures of diols and polyols. A capping agent, for example, trimethylolpropane or
45 diethanol amine is be used.

For the terminally stabilized polyurethane, the polyester diol preferably comprises between 20 and 80% by weight of the final polyurethane resin and generally has a molecular weight between 500 and 5,000, preferably between 1,000 and 3,500. Preferably, the polyester polyol component comprises between 50 and 70% and most preferably between 55 and 65% by weight of the polyurethane resin.

50 The terminally stabilized polyurethane resin may be comprised of the same weight percentages of the low molecular weight diol/triol component as the laterally stabilized polyurethane resin. Where these alcohol-containing compounds are mixed, it is preferred that the ratio of triol/diol be higher for the terminally stabilized polyurethane resins than in the case of laterally stabilized polyurethane resins.

The same weight percentages of polyisocyanate used in the laterally stabilized polyurethane are used
55 in the Terminally stabilized polyurethane. Preferably, the polyisocyanate is a diisocyanate comprising between 10 and 30% and most preferably between 10 and 20% by weight of the polyurethane.

In both the laterally stabilized and terminally stabilized polyurethane resins, the polyether component may be multi-functional (the functional groups being hydroxyls, thiols, or amines with hydroxyl groups

preferred), and preferably is a mono or di-functional polyether with monofunctional polyethers being particularly preferred. In general, water soluble polyether-containing compounds are useful in embodiments of the present invention. Polyethers formed from monoalcohol initiated polymerization of ethylene oxide, propylene oxide and mixtures, thereof are preferred. Of course, very minor amounts of butylene oxide ethers and other longer chain ethers may be incorporated into the polyether chain without adversely affecting the water dispersibility of the resins. Most preferably, ethylene oxide polymers comprise 100% of the polyether component. In general, the polyether containing component comprises between 2 and 40% by weight of the polyurethane, preferably between 8 and 30% by weight, and most preferably between 10 and 25% by weight of the final polyurethane resin.

The molecular weight of the polyether-containing compounds in general ranges from 500 to 7000, preferably ranges from 1000 to 4000, and most preferably ranges from 1200 to 3000.

The polyurethanes of the present invention are advantageously storage stable and are, of course, water dispersible. The water dispersibility of the resins is controlled by the amount of polyether character contained in the final resin particles and the hydrophobicity of the nonpolyether components.

DETAILED DESCRIPTION OF THE INVENTION

The laterally stabilized polyurethane resin is preferably comprised of the reaction product of:

- 1) a polyester polyol which is further comprised of the reaction product of a carboxylic acid-containing product having at least two carboxylic acid functionalities and a compound having at least two alcohol functionalities;
- 2) at least one low molecular weight compound having at least 2 alcohol functionalities;
- 3) at least one polyisocyanate-containing compound;
- 4) a nonionic stabilizer prepared by the reaction of a monofunctional ether with a polyisocyanate containing compound to produce a partially capped polyisocyanate followed by reaction with a compound containing at least one active amine hydrogen and at least two active hydroxyl groups and;
- 5) a capping agent is used to cap any remaining isocyanate groups that have not yet reacted.

The terminal stabilization polyurethane resin is preferably comprised of the reaction product of:

- 1) a polyester polyol;
- 2) at least one low molecular weight diol or triol;
- 3) a polyisocyanate;
- 4) a trihydroxy-containing monomer;
- 5) a monofunctional hydroxy-containing polyether; and
- 6) a capping agent.

The polyester component is not particularly critical to the present invention, but it is necessary that the polyester component be compatible with the desired waterdispersible characteristics of the resins described herein.

Thus, the carboxylic acid component of the polyester may be comprised of long-chain dicarboxylic acids, short-chain dicarboxylic acids, mixtures thereof or carboxylic acid equivalents such as anhydrides, lactones, and polycarbonates. Long-chain monocarboxylic acids may also be used, but these are generally employed to chain terminate the polyester resin.

The shorter chain carboxylic acid component, if used, may be comprised of a mono-, di- or higher functionality carboxylic acids or a mixture of these carboxylic acids having carbon chains of 18 or fewer carbon units. Monocarboxylic acids function to terminate a polyester chain and are chosen for that purpose.

It is preferable that the short chain carboxylic acid component be a dicarboxylic acid. Such preferred dicarboxylic acid compounds include, for example, adipic, azelaic, and other aliphatic dicarboxylic acids, however, any dicarboxylic acid-containing compound compatible with the goal of maximizing water-dispersibility may be utilized. Aromatic dicarboxylic acids may also be employed. An especially preferred aromatic dicarboxylic acid is isophthalic acid. Alkylene and aralkylene carboxylic acids may also be used. Where branched-chains in the polyester are desired, a carboxylic acid containing three or more carboxylic acid groups, for example citric acid, may be used. A preferred carboxylic acid-containing compound of this type is trimellitic anhydride.

The polyester resins are synthesized from the above-described carboxylic acid component and an excess of a polyol component. An excess of polyol is used so that the polyester resin preferably contains terminal hydroxyl groups. The polyol compounds preferably have an average hydroxy-functionality of at least 2.

The polyester resin in most cases is comprised of one or more polyols, preferably a diol. Up to 25 percent by weight of the polyol component may be a polyol having three or more hydroxy groups per

molecule. Where polyols having three or more hydroxy groups are chosen, the result is a branched polyester. As a general rule, the laterally stabilized polyurethane resin is comprised of a polyester having no more than 15 percent by weight of the alcohol-containing component of a polyol having three or more alcohol functionalities. The terminal stabilization polyurethane may be comprised of the same relative percentages of tri-alcohol containing component as that of the polyester utilized in the lateral stabilization polyurethane, or alternatively, may be comprised of a tri-alcohol-containing polyol of up to 25 percent by weight of the polyol component.

While it is not always desirable to have a triol or higher multi-functional alcohol present because of the tendency to form a branched chain polyester, some branching may be desirable, especially in the case where the polyester is to be incorporated into a branched polyurethane. There may also be present a small amount of monoalcohol in the polyol component, particularly if larger proportions of higher functional alcohols are used. These monoalcohols serve as chain terminators.

The diols which are usually employed in making the polyester resins include alkylene glycols, such as ethylene glycol, propylene glycol, butylene glycol, and neopentyl glycol, 1,6 hexanediol and other glycols such as hydrogenated bisphenol A, cyclohexane dimethanol, caprolactone diol (i.e., the reaction product of caprolactone and ethylene glycol) and hydroxyalkylated bisphenols. However, other diols of various types and, as indicated, polyols of higher functionality may also be utilized. Such higher functional alcohols can include, for example, trimethylolpropane, trimethylolethane and pentaerythritol as well as higher molecular weight polyols.

The low molecular weight diols which are preferred in the present invention are well known in the art. They have hydroxy values of 200 or above, usually within the range of 1500 to 2000. Such materials include aliphatic diols, particularly alkylene polyols containing from 2 to 18 carbon atoms. Examples include ethylene glycol, 1,4-butanediol, cycloaliphatic diols such as 1,2 cyclohexanediol and cyclohexane dimethanol. An especially preferred diol is 1,6 hexanediol.

To produce the laterally stabilized polyurethane resins which are useful in basecoat compositions of the present invention, the above-described polyester polyol is reacted with a mixture of a polyisocyanate, optionally a low molecular weight diol and/or triol, and a nonionic stabilizer comprised of, in part, a polyether containing compound. Two general synthetic approaches are utilized to synthesize the polyurethane resins of the present invention. The first approach is to react all products in one pot using an excess of hydroxy equivalents when synthesizing the polyurethane resin (capping occurs simultaneously with the synthesis of the polyurethane resin). Alternatively, an excess of isocyanate is utilized to form an intermediate polyurethane which is then capped with a capping agent such as trimethylol propane, diethanolamine, diols, or mixtures of diols or triols.

The polyester polyol, polyisocyanate, low molecular weight diols and/or triols, and nonionic stabilizer may be reacted in the same pot, or may be reacted sequentially, depending upon the desired results. Sequential reaction produces resins which are more ordered in structure. Both the polyester and triol containing compounds may serve as chain extenders to build up the polyurethane backbone through reaction of hydroxyl groups with isocyanate groups. Additional chain extenders having at least two active hydroxyl groups (diols, thiols, amines, or mixtures of these functional groups) may be added to increase the chain length or to change the chemical characteristics of the polyurethane resin. An excess of polyisocyanate is preferably used so that an intermediate polyurethane resin can be produced having free isocyanate groups at the ends. The free isocyanate groups may then be preferably capped with trimethylol propane or diethanolamine. The low molecular weight diols/triols/higher functional alcohols which are utilized as a separate component in synthesizing the polyurethane resins of the present invention include alkylene glycols, for example ethylene glycol, propylene glycol, butylene glycol, and neopentyl glycol. Additional alkylene glycols include cyclohexane dimethylol and caprolactone diol. Exemplary higher functional alcohols include trimethylol propane, trimethylolethane and pentaerythritol.

The organic polyisocyanate which is reacted with the polyester polyol and low molecular weight diol and/or triol material as described is essentially any polyisocyanate, i.e., any compound containing at least two isocyanate groups, and is preferably a diisocyanate, e.g., hydrocarbon diisocyanates or substituted hydrocarbon diisocyanates. Many such organic diisocyanates are known in the art, including p-phenylene diisocyanate, biphenyl 4,4'-diisocyanate, toluene diisocyanate, 3,3'-dimethyl-4,4 biphenylene diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethylhexane-1,6-diisocyanate, methylene bis (phenylisocyanate), 1,5 naphthalene diisocyanate, bis (isocyanatoethyl fumarate), isophorone diisocyanate (IPDI) and methylene-bis-(4 cyclohexylisocyanate). There can also be employed isocyanate-terminated adducts of diols, such as ethylene glycol, or 1,4-butylene glycol. These are formed by reacting more than one mol. of a diisocyanate, such as those mentioned, with one mol. of a diol to form a longer chain diisocyanate. Alternatively, the diol can be added along with the diisocyanate.

While diisocyanates are preferred, other multi functional isocyanates may be utilized. Examples are 1,2,4 benzene triisocyanate and polymethylene polyphenyl isocyanate.

It is preferred to employ an aliphatic diisocyanate, since it has been found that these provide better color stability in the finished coating. Examples include 1,6-hexamethylene diisocyanate, 1,4-butylene diisocyanate, methylene-bis-(4-cyclohexyl isocyanate) and isophorone diisocyanate. 2,4 toluene diisocyanates are also preferred. Mixtures of diisocyanates can also be employed.

The proportions of the diisocyanate, polyester, diol and/or triol component and nonionic stabilizer or monofunctional polyether are chosen so as to provide an isocyanate terminated intermediate polyurethane resin.

This can be accomplished by utilizing a stoichiometric excess of polyisocyanate, i.e., more than one isocyanate group per nucleophilic moiety (reactive with isocyanate) in the other components. The free isocyanates that remain after reaction are then capped with a capping agent, for example, trimethylol propane.

Longer-chain polyurethane resins may be obtained by chain extending the polyurethane chain with diol and/or triol-containing compounds. In addition, although it is not preferred, additional chain extending compounds having at least two active hydrogen groups for example diols, dithiols, diamines, or compounds having a mixture of hydroxyl, thiol, and amine groups, for example, alkanolamines, aminoalkyl mercaptans, and hydroxyalkyl mercaptans, may be used. For purposes of this aspect of the invention both primary and secondary amine groups are considered as having one active hydrogen. Alkanolamines, for example, ethanolamine or diethanolamine, may be used as chain extenders, and most preferably, a diol is used.

Examples of preferred diols which are used as polyurethane chain extenders include 1,6 hexane diol, cyclohexanedimethylol, and 1,4-butanediol. A particularly preferred diol is neopentylglycol. Polyhydroxy compounds containing at least three hydroxyl groups may also be used as chain extenders; the use of these compounds produces branched polyurethane resins. For purposes of the present invention, if it is preferred to minimize the amount of branching in the polyurethane resin these polyhydroxy compounds should be limited to a very minor component of the polyurethane producing mixture. These higher functional polyhydroxy compounds include, for example, trimethylolpropane, trimethylolethane and pentaerythritol.

The polyurethane resin may be chain extended in any manner using these diol and triol containing compounds or alternative compounds having at least two active hydrogen groups. Thus, these compounds may be added to the mixture of polyisocyanate, polyester, and polyether containing compound, (nonionic stabilizer or monofunctional polyether compound), or alternatively, may react at an intermediate stage, to link two free isocyanate groups that are present at the terminal ends of an intermediate polyurethane resin.

The polyether containing compounds, as described hereinabove, are preferably mono or di-functional polyethers with mono-functional polyethers being particularly preferred. The monofunctional polyethers are preferably formed from monoalcohol initiated polymerization of ethylene oxide, propylene oxide, and mixtures thereof. A polyether compound comprised of 100% ethylene oxide units is especially preferred. In its most preferred embodiment, the monofunctional polyether comprises between 10 and 25% by weight of the final polyurethane resin and has a molecular weight of between 1200 and 3000.

It is generally preferred that an intermediate polyurethane resin produced by reacting the polyester resin and the mixture of polyisocyanate, diol/triol mixture and polyether-containing compound be terminated with free isocyanate groups. To accomplish this, an excess of the polyisocyanate component is used. Thus, the diols/triols, polyether component and polyester diol will all react with isocyanate moieties to produce polyurethane resins having at least some free isocyanate groups. Of course, the molar ratio of the other components will be adjusted according to the desired characteristics of the intermediate and final polyurethane resins.

In one especially desirable embodiment of the invention, a multi-functional alcohol, for example, trimethylol propane is used to terminate the reaction (cap the free isocyanate groups) at the desired stage (determined by the viscosity and isocyanate groups present), thereby also contributing residual hydroxyl groups. Particularly desirable for such purposes are aminoalcohols, such as ethanolamine and diethanolamine, since the amino groups preferentially react with the isocyanate groups present. These capping agents are especially preferred for use in the grind resin aspect of the present invention. Multi-functional alcohols, such as ethylene glycol, trimethylolpropane and hydroxyl-terminated polyesters, can also be employed in this manner.

While the ratios of the components of the polyester, the multi-functional isocyanate, the diol/triol mixture, the polyether containing compounds, and the capping agent can be varied, it will be noted by those skilled in the art that the amounts should be chosen so as to avoid gelation and to produce an ungelled, urethane reaction product containing hydroxyl groups. The hydroxyl value of the final polyure-

thane reaction product should be at least 5 and preferably 20 to 200.

The amount of polyisocyanate used in the mixture is preferably between 10% and 30% by weight of the reactants in the mixture, and most preferably between 10 and 20%, but will vary depending upon the polyester used and the desired molecular weight of the final polyurethane resin. The amount of polyisocyanate will also vary depending upon whether it is desired to have the intermediate polyurethane terminated with free isocyanate groups or with hydroxyl groups. Thus, where it is preferred to terminate the intermediate polyurethane resin with free isocyanates for capping with trimethylolpropane or diethanolamine, an excess of polyisocyanate may be used. Where the intermediate polyurethane resin is to be terminated by hydroxyl groups, a stoichiometric deficiency of polyisocyanate may be used.

The polyurethane resins of the present invention are formulated, along with other components, into water dispersible basecoat compositions which are sprayed or electrostatically deposited onto metal or plastic substrates, for example, automobile bodies. In general, a polyurethane resin, formulated as described herein, is mixed with an aminoplast resin or a polyisocyanate, a grind resin, water, a portion of an organic solvent, pigments and a rheology control agent. Other agents may be included, for example, various fillers, surfactants, plasticizers, stabilizers, wetting agents, dispersing agents, defoamers, adhesion promoters and catalysts in minor amounts. In one embodiment a branched-chain polyester component may also be added to the basecoat composition.

As indicated, an aqueous dispersion of the polyurethane resin is utilized as the principal or major vehicle resin. In general, the principal or major vehicle resin comprises between 0 and 90% by weight of the total solids present in the basecoat composition. An acceptable polyurethane resin for use as the principal resin is a resin produced from a polyester synthesized from dimer fatty acid, isophthalic acid, and 1,6 hexanediol. The resulting polyester is then reacted with a diisocyanate of isophorone, a triol and a polyether monoalcohol and a diol, for example, neopentyl glycol. The resulting polyurethane intermediate having free isocyanate groups is then reacted with trimethylolpropane to cap these groups.

The polyurethane reaction product as described above may be mixed with an aminoplast resin or a polyisocyanate cross-linking agent. Aminoplast resins are aldehyde condensation products of melamine, urea, and similar compounds. Products obtained from the reaction of formaldehyde with melamine, urea or benzoguanamine are most common and are preferred herein. However, condensation products of other amines and amides can also be employed, for example, aldehyde condensates of triazines, diazines, triazoles, guanidines, guanamines and alkyl and aryl substituted derivatives of such compounds, including alkyl and aryl substituted ureas and alkyl and aryl substituted melamines. Some examples of such compounds are N,N'-dimethylurea, benzourea, dicyandiamide, formoguanamine acetoguanamine, ameline, 2-chloro-4,6-diamino-1,3,5-triazine, 6-methyl-2,4-diamino-1,3,5-triazine, 3-5-diamino-triazole, triaminopyrimidine, 2-mercapto-4,6 diaminopyrimidine and 2,4,6-triethyl triamino-1,3,5-triazine.

While the aldehyde employed is most often formaldehyde, other similar condensation products can be made from other aldehydes, for example, acetaldehyde, crotonaldehyde, acrolein, benzaldehyde and furfural.

The amine-aldehyde condensation products may contain methylol or similar alkylol groups, and in most instances at least a portion of these alkylol groups are etherified by a reaction with an alcohol to provide organic solvent-soluble resins. Any monohydric alcohol can be employed for this purpose, including such alcohols as methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, as well as benzyl alcohol and aromatic alcohols, cyclic alcohols, for example, cyclohexanol, monoethers or glycols such as Cellosolves® and Carbitols® (Union Carbide), and halogen-substituted or other substituted alcohols, such as 3-chloropropanol.

The preferred amine-aldehyde resins are etherified with methanol or butanol.

Alternatively, isocyanate-containing compounds such as those previously described may be used as cross-linking agents. Generally, when polyisocyanates are used they comprise between 1 and 50% of the basecoat composition. Preferably, a fully blocked polyisocyanate is used as a crosslinking agent.

In the preparation of the blocked organic polyisocyanate any suitable organic polyisocyanate may be used. Examples include the aliphatic compounds such as trimethylene, tetramethylene, hexamethylene, 1,2-propylene, 1,2-butylene, 2,3-butylene, 1,3-butylene, ethylidene and butylidene diisocyanates; the cycloalkylene compounds such as 1,3 cyclopentane, 1,4-cyclohexane, and 1,2-cyclohexane diisocyanates; the aromatic compounds such as an phenylene, p-phenylene, 4,4'-diphenyl, 1,5-naphthalene and 1,4-naphthalene diisocyanates, the aliphatic-aromatic compounds such as 4,4' diphenylene methane, 2,4 or 2,6-tolylene, or mixtures thereof, 4,4', toluidine, and 1,4-xylylene diisocyanates; the nuclear substituted aromatic compounds such as dianisidine diisocyanate, 4,4'-diphenylether diisocyanate and chlorodiphenylene diisocyanate, the triisocyanates such as triphenyl methane-4,4; 4''-triisocyanate, 1,3,5-trisocyanate benzene and 2,4,6-triisocyanate toluene; and the tetraisocyanates such as 4,4'-diphenyl-dimethyl methane 2,2', 5,5'-

tetraisocyanate; the polymerized polyisocyanates such as tolylene diisocyanate dimers and trimers.

Any suitable aliphatic, cycloaliphatic aromatic alkyl monoalcohol and phenolic compound may be used as blocking agent in accordance with the present invention, such as for example, lower aliphatic alcohols, such as methyl, ethyl, chloroethyl, propyl, butyl, cyclohexyl, heptyl, octyl, nonyl 3,3,5-trimethylhexanol, decyl and lauryl alcohols, the aromatic alkyl alcohols, such as phenylcarbinol, methylphenylcarbinol, ethyl glycol monoethyl ether, and ethyl glycol monobutyl ether; the phenolic compounds such as phenol itself, substituted phenols in which the substituents do not adversely affect the coating operations. Examples include cresol, xyleneol, nitrophenol, chlorophenol, ethylphenol, 1-butyl phenol and 2,5-di-t-butyl- 4-hydroxy toluene. Minor amounts of even higher molecular weight relatively nonvolatile monoalcohols may also be used.

Additional blocking agents include tertiary hydroxyl amines such as diethylethanolamine and oximes such as methylethyl ketone oxime, acetone oxime and cyclohexanone oxime. Use of oximes and phenols is particularly useful because specific polyisocyanates blocked with these agents uncap at relatively low temperatures without the need for externally added urethane forming catalysts such as those described below.

The organic polyisocyanate-blocking agent adduct is formed by reacting a sufficient quantity of blocking agent with the organic polyisocyanate to insure that no free isocyanate groups are present.

A grind resin may also be used in the basecoat compositions of the present invention. The grind resin may be comprised of a number of water soluble polyurethane resins, which may be different in chemical character to the principal or major vehicle resin, e.g., in a particular basecoat formulation a terminally stabilized polyurethane compound may be used as the principal resin and a laterally stabilized polyurethane resin be used as the grind resin. Both laterally stabilized and terminally stabilized nonionic polyurethane resins of this invention may be used as grind resins to formulate paint. The grind resin may range between 2 and 25% by weight of the total solids in the coating composition and preferably comprises 5-40% by weight of the basecoat composition.

Pigments may be incorporated into the basecoat composition to provide the desired cosmetic characteristics. This is done by mixing pigments with the above-described grind resin, and in addition, optionally, aminoplast resin to form a pigment paste. In a preferred embodiment, the methodology of preparing a pigment paste with the nonionic polyurethane resins of the present invention has been simplified in comparison to that used to make pigment paste with anionic polyurethane resins. In this method, the nonionic polyurethane resin is simply mixed with pigment. Aminoplast cross-linking agents may also be added, but such addition is not preferred.

The final pigment paste comprises 3% to 65% by weight of a pigment, and 5% to 65% by weight of a laterally terminally stabilized polyurethane resin and optionally, up to 50% by weight of a cross-linking agent.

Any standard pigment known in the art may be used with resins of the present invention so long as these pigments can be formulated without affecting the desired characteristics of the resins. Specific examples of the dye stuffs or pigments may be inorganic or organic, for example, graphite, carbon black, zinc chromate, strontium chromate, barium chromate, lead chromate, lead cyanide, titanium dioxide, zinc oxide, cadmium sulfide, iron oxide, aluminum flakes, zinc sulfide, phthalocyanine complexes, naphthol red, quinacridones and halogenated thioindigo pigments.

Preferred aluminum flake pigments are available from Silberline Corp, Lansford, Pennsylvania or from Eckart Werke, Gunterstahl, West Germany. The aluminum flake pigments provide the coating with an enhanced "metallic veneer". In a preferred embodiment of the present invention standard grade aluminum stabilized with phosphate ester is used. Other metallic flake pigments, for example, silver may also be used. The metallic pigments may also be mixed with non-metallic pigments, but these are to be carefully chosen so as not to diminish the desired metallic effect.

The resinous dispersions of the basecoat compositions are dispersed in deionized water. It is preferred that the deionized water have conductance readings of less than 13×10^{-6} ohms⁻¹ (13 microohms⁻¹) and most preferably less than 5×10^{-6} ohms⁻¹ (5 microohms⁻¹) to prevent gassing caused by the reaction of aluminum with water. Deionized water is also chosen to avoid salts that naturally occur in tap water. Other solvents may also be employed with the deionized water. An especially preferred solvent is Butyl Cellosolve^R which aids mixing, formulating and dispersing pigment in the basecoat composition. Other solvents can also be used, for example, low-boiling mono and polyhydric alcohols, ethers, esters, ketones and other organics. The organic solvent, which comprises at most 80% of the basecoat composition, and preferably comprises 10 to 20% by weight of the basecoat composition (including water) may be selected to promote the dispersibility of individual components in the final basecoat composition (plasticizer characteristics) and for its low volatility characteristics.

A rheology control agent is also preferably incorporated into the basecoat composition. The rheology control agent controls the viscosity of the resulting composition and is incorporated in amounts that will prevent sagging or running after a basecoat is sprayed onto a vertical surface such as an automobile body. The direct result of incorporating a rheology control agent is to provide flow control, body and sprayability.

Another favorable result of adding a rheology control agent is to allow for the deposition of a thicker coating, allowing more complete coverage of a substrate. The sprayed coatings containing these agents also exhibit greater orientation of the flake pigments on the final coated substrate. Rheology control agents which can be used in embodiments of the present invention include the fumed silica compounds and the bentonite clays. Preferred fumed silica compounds are the hydrophobic silica compounds, for example Aerosil^R R972, available from Degussa Corporation, (Frankfurt, West Germany). Another rheology control agent which may be used, and in certain basecoat compositions, may be preferred is a synthetic sodium lithium magnesium silicate hectorite clay. An example of one such clay is Laponite^R RD, available from Laporte, Inc (Saddlebrook, Jersey). In certain preferred embodiments rheology control agents are mixed. The rheology control agent when it is included, generally comprises from 0% to 20 percent by weight of the basecoat composition and preferably comprises between 1 percent and 5 percent by weight of the final basecoat composition.

In general, the particle size of the rheology control agent plays a role in the overall thixotropic properties of these resins. Rheology control agents in embodiments of this invention are suspended in the material. It may be proposed that the suspended rheology control agents function, at least in part, through coulombic or electrostatic interactions.

In general, the particle sizes can be from less than 0,01 μm (0.01 microns) to over 200 μm (200 microns). These sizes can be adapted to develop in part the rheology properties sought. In appropriate circumstances, the particle sizes may be from about 1 to about 10 μm .

Any additional agent used, for example, surfactants, fillers, stabilizers, wetting agents, dispersing agents, adhesion promoters, etc. may be incorporated into the basecoat composition. While the agents are well-known in the prior art, the amount used must be carefully controlled to avoid adversely affecting the coating and quick-drying characteristics.

The final basecoat composition is adjusted to a pH of between 6.0 and 8.0. Viscosity may be adjusted using deionized water. Final basecoat compositions are comprised of the following components in the indicated weight ratios.

Table I

General Description of a Silver Metallic Paint	
Ingredient	Amount (% by weight of Solids of Final Basecoat composition)
Polyurethane resin	20-80%
Melamine	5-50%
Rheology Control Agent	0-20%
Pigment (Includes Aluminum Flakes)	0-20%
Acid Catalyst	0-5%

The basecoat compositions described hereinabove can be applied to a metal or plastic substrate in one or two coats using for example an air atomizer (Binks Model 60 spray gun, available from Binks Manufacturing Corporation, (Franklin Park, Illinois), or by using other conventional spraying means. The basecoat compositions are preferably sprayed at 3,45 - 5,51 bar (50-80psi), and a relative humidity of between 50 and 90% (optimally at 60-80% relative humidity) and a temperature of 21 - 32 °C (70-90 °F).

After being deposited, the basecoat compositions are flash dried within a temperature range of about room temperatures to 63 °C (145 degrees F). The preferred flash temperature is 49 °C (120 degrees F). The flash conditions described herein result in about 90% of the solvents (water plus organics) being flashed from the basecoat in this short period of time.

After the first basecoat is deposited, a second basecoat can be deposited over the first without drying (flash off), or alternatively, a clearcoat may be deposited over the flashed basecoat. It is a surprising result of the use of the nonionic resins of the present invention that when straight shade (non-metallic) or metallic pigments are used, one coat of basecoat might be used to provide excellent cosmetic characteristics. Any number of clearcoat compositions known in the art may be used. Any known unpigmented or other transparently pigmented coating agent is in principle, suitable for use as a topcoat. A typical top coat

composition contains 30-60% film forming resin and 40-70% volatile organic solvent.

After the clear coat is coated onto the basecoat layer, the multi-layer coating is then baked to cross-link the polymeric vehicle and to drive the small amount of residual water and organic solvent from the multi-layered polymeric composition. A preferred baking step involves heating the coated substrate for a period of 10-60 minutes at a temperature of between 66 and 149 °C (150 and 300 degrees F). The baking step cures the coating to a hard, durable film.

The final multi-layer coated substrate comprises:

- a) a waterborne basecoat composition comprising about 20 to about 80% by weight of said basecoat composition of a polyurethane composition;
- b) about 5% to about 50% by weight of a cross-linking agent;
- c) optionally, up to about 20% by weight of a rheology control agent;
- d) about 5% to about 65% by weight of a pigment paste; and
- e) a clear top coat.

The invention will be further described in connection with several examples which follow. These examples are shown by way of illustration of the invention and are not meant to limit the scope of the invention. All parts and percentages in the examples are by weight unless otherwise indicated.

Example 1: Preparation of Polyester Resin A

A polyester polyol resin is prepared by charging a reaction vessel flask equipped with a fractionating column, with 551.9 g (15.8% of the polyester resin) of isophthalic acid, 1923 g (54.9%) Empol[®] 1010 (dimer fatty acid available from Emery Chemical Co.), and 1025.1 g (29.3%) of 1,6 hexanediol and 100 g of toluene. Additional toluene may be added to fill the trap. The mixture was heated under nitrogen and the water of condensation was removed. During this heating 235.7 g of water is distilled off. Heating was continued at approximately 200 degrees C until the acid number is less than or equal to 8. The remaining toluene is then vacuum stripped at 200 °C to produce a polyester resin for use in the polyurethane resin.

Example 2: Preparation of Polyester B

A reaction vessel is charged with 960.0 g (43.5 WGT %) of neopentyl glycol, 664.6 g (30.1 WGT %) of isophthalic acid, 584.7 g (26.5 WGT %) of adipic acid, and 50.0 g of toluene. The mixture is heated under nitrogen to 240 °C until an acid number of 3.5 is reached.

Example 3: Preparation of Terminally Stabilized Polyurethane Resin

42.0 g of methoxy polyethylene oxide of 2000 equivalent weight, 88.5 g of IPDI, and 50.0 g of glycol ether PM acetate are charged to a reactor and heated to 95 °C for 2 hours under nitrogen. The mixture is cooled to 30 °C, then 252.0 g of polyester A, 9.7 g of neopentyl glycol, and 25.0 g of trimethylolpropane are added. The mixture is heated to 110 °C until all NCO groups have reacted. The mixture is cooled to 80 °C then 90.0 g of isopropanol is added. The mixture is further cooled to 68 °C and 420.0 g of deionized water is added in under vigorous agitation over 10 minutes. The resulting dispersion has a solids content of 42.4% and an average particle size of 140 nm.

Example 4: Preparation of Terminally Stabilized Polyurethane Resin

44.1 g of a butanol-initiated random copolymer of 75% ethylene oxide and 25% propylene oxide of 2100 equivalent weight, 88.5 g of IPDI, and 50.0 g of glycol ether PM acetate are charged to a reactor and heated to 95 °C for 2 hours under nitrogen. The mixture is allowed to cool to 30 °C and 260.6 g of polyester A, 9.7 g of neopentyl glycol, and 25.0 g of TMP are added. The mixture is heated to 100 °C until all NCO groups have reacted. The mixture is cooled to 82 °C and 90.0 g of isopropanol is added in. The mixture is further cooled to 57 °C and 420.0 g of deionized water is added in under vigorous agitation over 1 hour. The resulting dispersion has a solids content of 43.0% and an average particle size of 190 nm.

Example 5a: Preparation of Laterally Stabilized Polyurethane Resin

Linear Nonionic PE/PU "Principle Resin"

5 PREPARATION OF A METHOXYPOLYETHER DIOL

A carbowax diol is prepared by charging a flask with 4538 grams of methoxypolyethylene glycol 2000 and 1015 grams of toluene. The mixture is heated to reflux to remove the water present in the carbowax. When all the water has been removed the temperature of the batch is lowered to 50 °C and 4.5 grams of benzoyl chloride is added and allowed to mix for 10 minutes. At this point 394.7 g of toluene diisocyanate is added to the flask and heated to 70 °C and held until the appropriate isocyanate value is reached. The heat is turned off and 249 grams of diethanolamine is added to the flask. When the exotherm has ended the batch is held 10 minutes. Then a vacuum strip is started to remove all the toluene. Once all the toluene is removed, the diol is ready to be used in the polyurethane formation.

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PREPARATION OF A POLYURETHANE RESIN

A flask is charged with 600 grams of polyester A (example = 1), 100 grams of carbowax diol, 50.2 grams of neopentyl glycol, 249.8 grams of isophorone diisocyanate, and 205 grams of propylene glycol monomethyl ether acetate. The mixture is heated to 125 °C and reacted to a constant isocyanate value. Then 44.8 grams of trimethylolpropane is added and reacted for 1 hour at 125 degrees C. Then the batch is cooled to 110 °C and 362.2 grams of ethylene glycol monobutyl ether is added. Then 1632.2 grams of deionized water is added under high agitation to form a dispersion.

25 Example 5B: GRIND RESIN - LATERALLY STABILIZED NON-IONIC PE/PU

PREPARATION OF A CARBOWAX DIOL

A carbowax diol is prepared by charging a flask with 4538 grams of methoxypolyethylene glycol 2000 and 1015 grams of toluene. The mixture is heated to reflux to remove the water present in the carbowax. When all the water has been removed the temperature of the batch is lowered to 50 °C and 4.5 grams of benzoyl chloride is added and allowed to mix for 10 minutes. At this point 394.76 grams of toluene diisocyanate is added to the flask and it is heated to 70 °C and held there until the appropriate isocyanate value is reached. The heat is turned off and 249 grams of diethanolamine is added to the flask. When the exotherm has ended the batch is held for 10 minutes. Then a vacuum strip is started to remove all the toluene. Once all the toluene is removed, the diol is ready to be used in polyurethane formation.

PREPARATION OF A POLYURETHANE RESIN

A flask is charged with 600 grams of polyester A (example = 1), 100 grams of carbowax diol, 50.2 grams of neopentyl glycol, 249.8 grams of isophorone diisocyanate, and 205 grams of propylene glycol monomethyl ether acetate. The mixture is heated to 125 °C and reacted to a constant isocyanate value. Then the batch is cooled to 110 °C and 35 grams of diethanolamine is added. Then 1632.2 grams of deionized water is added under high agitation to form a dispersion.

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Example 6: Preparation of a Terminally stabilized Polyurethane Resin

643.5 g of polyester A, 201.0g of methanol-initiated polyethylene oxide of 1350 equivalent weight, 145.0 g of IPDI, and 175.0 g of MPK are charged to a reactor and heated to 124 °C under nitrogen until a constant NCO equivalent value is obtained. Next, 25.8 g of TMP is added and heating to 124 °C was resumed. After 2 hours reaction time, all NCO groups have reacted, and 255.0 g of monobutyl glycol ether is added. The mixture is cooled to 80 °C and 1775 g of deionized water is added in over 10 minutes under vigorous agitation. The resulting dispersion has a solids content of 31.3% and an average particle size of 60 nm.

55 Example 7: Preparation of Terminally Stabilized polyurethane resin

455.0 g of polyester B, 155.0 g of methanol-initiated polyethylene oxide of 1450 equivalent weight, 10.0 g of TMP, 131.0 g of IPDI, and 132.0 g of MPK are charged to a reactor and heated to 105 °C under

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nitrogen for six hours, at which time no NCO groups remain unreacted. 200.0 g of monobutyl glycol ether is added and the mixture is cooled to 70 °C. Next, 1370.0 g of deionized water is added in over 10 minutes under vigorous agitation. The resulting dispersion has a solids content of 31.5% and a Gardner viscosity of E.

Example 8: Preparation of silver metallic basecoat using laterally stabilized nonionic resin

Components	Parts by Weight	WGT % NV
2% Laponite ^R paste	242.2	3.2
Resin from example 5	201.1	47.7
Aluminum paste (ALCOA ^R 87575)	32.9	14.9
Phosphate ester solution	1.4	
Melamine (Cymel ^R 303)	51.1	44.5
p-Toluenesulfonic acid catalyst (amine blocked)	9.1	1.5
deionized water	162.2	

The polyurethane resin from example 5 is slowly added to the 2% Laponite^R paste under vigorous agitation. In a separate container the aluminum slurry is prepared by mixing the aluminum paste, phosphate ester solution, and melamine under agitation. The aluminum slurry is slowly added to the resin mixture under high agitation. Deionized water is added to reduce the viscosity of the paint to 14 seconds (#2 FISHER CUP). The pH of the paint is 6.7.

Example 9: Preparation of silver metallic basecoat using terminal stabilization nonionic resin

The paint is prepared according to the process of example 8 except the terminally stabilized polyurethane resin of example 4 is used. The paint has a viscosity of 14 seconds (#2 FISHER CUP).

Comparison study: Lateral stabilization vs. terminal stabilization silver metallic basecoats

The silver metallic basecoats from examples 8 and 9 were sprayed side-by-side using a siphon automatic spray gun. Both paints were sprayed at 4.48 bar (65 psi) over primed steel panels at 28 °C (82 °F) and 44% relative humidity. The panels were baked at 121 °C (250 degrees F) for 30 minutes and the metallic effect was evaluated by comparison with a series of five standard silver metallic panels (1 = best). Results were as follows:

Silver Paint	Metallic Effect (1 = best)
example 8	3.0
example 9	5.0

The silver metallic basecoats from examples 8 and 9 were resprayed at 20 °C (68 degrees F) and 80% relative humidity to test for the sag resistance of the paint. After baking the panels for 30 minutes at 121 °C (250 degrees F), a relative sag resistance value was assigned to each panel (1 = best; no sag, 5 = worst; excessive sag). Results are as follows:

Silver Paint	Sag Resistance (1 = best)
Example 8	1
Example 9	5

The following examples of pigment grind pastes and straight-shade paint are applicable to both types of urethanes (i.e., lateral stabilization and terminal stabilization).

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Example 11: Preparation of a TiO₂ pigment paste

Dispersion of TiO₂

The nonionic urethane dispersions have been used to mill TiO₂ for example, as supplied by DuPont, Glidden, etc., and more specifically, using DuPont R960HGHG as in the example below:

	Grams	Grams Non-Volatile
Nonionic Urethane Dispersion	1452	450
DuPont R960HGHG	2250	2250
Deionized Water	331	

The urethane dispersion is placed in a two gallon vessel equipped with a propeller type agitator. The dry TiO₂ is added to the stirred dispersion. Deionized water is used to maintain a fluid paste. After the pigment is added, the slurry is stirred for 30 minutes. The viscosity is adjusted to 75-95 Krebs units (7-15 dPa s (700-1500 cps)) with water. Stirring is continued for 15 minutes. The paste is fed through a gravity fed sandmill as obtained from Chicago Boiler Company, charged with ceramic or glass media. Particle sizes of 0 - 6.5 μ m (0-6.5 microns) is reached in one or two passes.

Example 12: Preparation of a Blue Pigment Paste

Dispersion of Phthalocyanine Blue Pigments

The nonionic urethane dispersions have been used to mill phthalocyanine pigments for example, those supplied by Ciba Geigy, Toyo Ink, Sun Chemical, etc., and more specifically Ciba Geigy X3485 as in the example below:

	Grams	Grams Non-Volatile
Nonionic urethane dispersion	1781	552
ciba Geigy X3485	276	276

The urethane dispersion is placed in a two gallon vessel equipped with a propeller type agitator. The dry pigment is added to the stirred dispersion. After the addition of the pigment, the slurry is stirred 30 minutes. Deionized water may be added if necessary to achieve a viscosity of 60-85 Krebs units (5-10 dPa s (500-1000 cps)). Stirring is then continued for 15 minutes. The paste is then fed through a gravity fed sandmill as described above until the particle size is 0-12 μ m (0-12 microns).

Example 13: Preparation of a Perylene Pigment Paste

Dispersion of Perylene Pigments

The nonionic urethane dispersions have been used to mill perylene pigments as supplied by Mobay, BASF, etc., more specifically Mobay R6424 in the example below:

	Grams	Grams Non-Volatile
Nonionic urethane dispersion	2419	774
Mobay R6424	581	581
Deionized Water	109	581

The urethane dispersion is charged into a two gallon vessel equipped with a propeller type agitator. The dry pigment is added to the stirred dispersion. Stirring is continued for 30 minutes after the pigment has been added. Deionized water is used to obtain a viscosity of 50-85 Krebs units (2-10 dPa s (200-1000 cps)). The slurry is then added to an attritor as supplied by Union Process, Akron, Ohio, charged with stainless steel shot. After 4-8 hours the particle size is 0-6.5 μ m (0-6.5 microns).

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Example 14: Preparation of a Carbon Black Pigment Paste

Dispersion of Carbon Black Pigments

- 5 The nonionic urethane dispersions have been used to mill carbon black pigments from Degussa, Columbian Chemicals, Cabot, etc., more specifically Cabot Black Pearls 1300 in the example below:

		Grams	Grams Non-Volatile
10	Nonionic Urethane Dispersion	2800	896
	Cabot Black Pearls 1300	224	224

- 15 The urethane aspersions are charged with a two gallon vessel equipped with a propeller type agitator. The dry pigment is added to the dispersion. Stirring is continued for 30 minutes after the pigment has been added. If necessary deionized water is used to obtain a viscosity of 50-85 Krebs units (2-10 dPa s (200-1000 cps)). The slurry is then added to an attritor as supplied by Union Process, Akron, Ohio, charged with stainless steel shot. After 4-8 hours the particle size is 6-12 μ m (6-12 microns).

20 Example 15: Preparation of a Nonionic White Basecoat

		#Pigment	#Vehicle	100#
25	A) Laponite ^R Plurion ^R P900 DI H ₂ O Total for A	2	2	13.9
30	B) Melamine (Cymel ^R 303) Butyl Cellosolve		31.4	6.35 1.62
	C) Nonionic urethane Dispersion		33.5	21.7
35	D) Fumed Silica (R-972 from Degussa) Melamine Nonionic dispersion Total	9.5	4.61 8.74	16.2
	E) White grind paste (Example 11) F) Oxazolidine blocked pTSA	100.0	19.8 2.29	38.2 1.91

- 40 Part A is mixed under high agitation for 2 hours. Part B is added slowly under agitation followed by Part C.

- Part D is ground separately in a mill and it and parts E and F are added under agitation. Final adjustments in viscosity are made with deionized water. The pH of the basecoat is 6.0-8.0.

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Claims

1. A method of coating a substrate with a multi-layer coating comprising
- (A) applying onto the substrate a first layer of waterborne basecoat composition comprising
- 50 a) a water-dispersible polyurethane resin wherein said polyurethane resin has an hydroxyl value of at least 5 and comprises the isocyanate group-free reaction product of
- 1) a polyurethane resin having at least some free isocyanate groups that is the reaction product of
- 55 1) at least one polyester polyol, and optionally at least one diol and/or triol having hydroxy values of 200 or above
- 2) at least one nonionic stabilizer that is a monofunctional polyether or is the reaction product of

- i) a polyether half-capped diisocyanate intermediate formed by the reaction of a monofunctional polyether with a diisocyanate, and
- ii) a compound having at least one active amine hydrogen reactive with isocyanate groups and at least two active hydroxyl groups reactive with isocyanate groups, and
- 5 3) an excess of at least one polyisocyanate, and
- II) at least one diol, triol or aminoalcohol capping agent to cap said free isocyanate groups, and
- b) an aminoplast resin or a polyisocyanate crosslinking agent, and
- (B) flash drying said first layer within a temperature range of room temperature to 63 °C,
- (C) applying at least one layer of a clear top coat onto said basecoat, and
- 10 (D) baking said multi-layer coating to crosslink the coating to a hard durable film.

- 2. A method according to claim 1 wherein said water-dispersible polyurethane resin is utilized as the principal resin.
- 15 3. A method according to claim 1 or 2 wherein said water-dispersible polyurethane resin is utilized as a grind resin.
- 4. A method according to claims 1 to 3 wherein the monofunctional polyether is formed from monoalcohol initiated polymerisation of ethylene oxide, propylene oxide and mixtures thereof and has a molecular weight between 500 and 7.000.
- 20 5. A method according to claim 1 to 4 wherein said polyisocyanate 3) is an aliphatic diisocyanate or a mixture of aliphatic diisocyanates.

25 Patentansprüche

- 1. Verfahren zum Lackieren eines Substrats mit einem Mehrschichtlack, bei dem man
 - (A) auf das Substrat eine erste Schicht aus einer wäßrigen Basislackzusammensetzung bestehend aus
 - 30 (a) einem wasserdispergierbaren Polyurethanharz, worin das Polyurethanharz eine Hydroxylzahl von mindestens 5 aufweist und aus dem von Isocyanatgruppen freien Umsetzungsprodukt aus
 - I) einem Polyurethanharz mit mindestens einigen freien Isocyanatgruppen, bei dem es sich um das Umsetzungsprodukt aus
 - 1) mindestens einem Polyester-Polyol und gegebenenfalls mindestens einem Diol und/oder Triol mit Hydroxylzahlen von 200 oder darüber,
 - 2) mindestens einem nichtionischen Stabilisator, bei dem es sich um einen monofunktionellen Polyether oder um das Umsetzungsprodukt aus
 - i) einer Zwischenstufe aus einem mit Polyether halbmaskierten Diisocyanat, die durch Umsetzung eines monofunktionellen Polyethers und einem Diisocyanat erhalten wurde, und
 - 40 ii) einer Verbindung mit mindestens einem gegenüber Isocyanatgruppen reaktiven, aktiven Aminwasserstoff und mindestens zwei gegenüber Isocyanatgruppen reaktiven, aktiven Hydroxylgruppen handelt, sowie
 - 3) einem Überschuß an mindestens einem Polyisocyanat handelt,
 - 45 II) mindestens einem Maskierungsmittel aus Diol, Triol oder Aminoalkohol zur Maskierung der freien Isocyanatgruppen, sowie
 - b) einem Aminoharz oder einem Polyisocyanat als Vernetzungsmittel aufträgt,
 - (B) diese erste Schicht in einem Temperaturbereich von Raumtemperatur bis 63 °C ablüftet,
 - (C) auf diesen Basislack mindestens eine Schicht aus einem Klardecklack aufträgt und
 - 50 (D) den Mehrschichtlack zwecks Vernetzung des Lacks zu einem harten dauerhaften Film einbrennt.
- 2. Verfahren nach Anspruch 1, wobei das wasserdispergierbare Polyurethanharz als Hauptharz verwendet wird.
- 55 3. Verfahren nach Anspruch 1 oder 2, wobei das wasserdispergierbare Polyurethanharz als Anreibharz verwendet wird.

4. Verfahren nach Ansprüchen 1 bis 3, wobei der monofunktionelle Polyether durch mit einem Monoalkohol initiierte Polymersiation von Ethylenoxid, Propylenoxid und deren Mischungen gebildet wird und ein Molekulargewicht zwischen 500 und 7000 besitzt.
5. Verfahren nach Ansprüchen 1 bis 4, wobei das Polyisocyanat 3) ein aliphatisches Diisocyanat oder eine Mischung aus aliphatischen Diisocyanaten ist.

Revendications

1. Procédé pour revêtir un substrat d'un revêtement multicouche, comprenant:
(A) l'application, sur le substrat, d'une première couche de composition de couche de base à l'eau comprenant:
a) une résine de polyuréthane dispersable dans l'eau, dans laquelle ladite résine de polyuréthane possède un indice d'hydroxyle d'au moins 5 et comprend le produit de réaction, dépourvu de groupes isocyanate,
I) d'une résine de polyuréthane possédant au moins quelques groupes isocyanate libres, qui est le produit de réaction
1) d'au moins un polyester-polyol, et éventuellement d'au moins un diol et/ou un triol, ayant des indices d'hydroxyle de 200 ou plus,
2) d'au moins un stabilisant non ionique qui est un polyéther monofonctionnel ou qui est le produit de réaction
i) d'un intermédiaire diisocyanate semi-coiffé par un polyéther, formé par réaction d'un polyéther monofonctionnel avec un diisocyanate, et
ii) d'un composé possédant au moins un atome d'hydrogène d'amine réactif avec les groupes isocyanate et au moins deux groupes hydroxyle actifs, réactifs avec les groupes isocyanate, et
3) d'un excès d'au moins un polyisocyanate, et
II) d'au moins un agent coiffant diol, triol ou aminoalcool, pour coiffer lesdits groupes isocyanate libres, et
b) une résine aminoplaste ou un agent de réticulation polyisocyanate, et
(B) le séchage éclair de ladite première couche, dans une gamme de températures allant de la température ambiante à 63 °C, et
(C) l'application d'au moins une couche de vernis de finition sur ladite couche de base, et
(D) la cuisson dudit revêtement multicouche pour réticuler le revêtement afin de donner un film dur durable.
2. Procédé selon la revendication 1, dans lequel ladite résine de polyuréthane dispersable dans l'eau est utilisée comme résine principale.
3. Procédé selon la revendication 1 ou 2, dans lequel ladite résine de polyuréthane dispersable dans l'eau est utilisée comme résine à broyer.
4. Procédé selon les revendications 1 à 3, dans lequel le polyéther monofonctionnel est formé par polymérisation, initiée par un monoalcool, d'oxyde d'éthylène, d'oxyde de propylène et de mélanges de ceux-ci, et possède une masse moléculaire comprise entre 500 et 7 000.
5. Procédé selon les revendications 1 à 4, dans lequel ledit polyisocyanate 3) est un diisocyanate aliphatique ou un mélange de diisocyanates aliphatiques.